CHARACTERIZATION OF POLYMERIZED IONIC LIQUIDS-BASED HYDROGELS

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ABSTRACT

Polymerized Ionic Liquids (PILs) are hydrogels synthesized from ionic liquids. They combine the positive characteristics of ionic liquids and polymers which is why they have a wide range of applications, e.g. in the pharmaceutical sector. They are characterized by properties such as high mechanical strength, biocompatibility, and favorable swelling behavior. In this study, the extremely high mechanical strength of novel polymerized ionic liquids (PILs)-based hydrogels was confirmed by mechanical tests. The swelling behavior was studied of hydrogels based on 1-Vinyl-3-alkylimidazolium bromide with different crosslinkers in various solvents – aqueous and organic.

Keywords: Hydrogel, Polymerized Ionic Liquids, Swelling Properties, Mechanical Properties

INTRODUCTION

Hydrogels are a unique class of polymeric materials that have a three-dimensional network structure which can absorb and retain large amounts – from few percent to thousands of times their dry weight – of water without dissolving. The insolubility as well as mechanical properties or swelling behavior are due to the chemical and/or physical crosslinker and its amount [Hussain, 2013]. Furthermore, there are hydrogels with a number of useful properties such as self-healing or biocompatibility [Ahmed, 2015]. Due to the favorable properties of hydrogels, there are numerous applications of hydrogels in medical and pharmaceutical fields, as contact lenses, as materials for artificial skin or drug delivery systems, but they also have potential applications as immobilization matrices for e.g. enzymes and catalysts [Grollmisch, 2018] or in other fields.

Most Hydrogels, which include polymerized ionic liquids (PILs) are formed by click-chemistry [Boehnke, 2015]. This has the advantage of no undesirable by-products being formed. The remaining PILs combine the features of ILs (e.g., ionic conductivity, thermal, and chemical stability, tunable solution properties) and the properties of polymers [Eftekhari, 2017].

For all the applications mentioned, however, it is crucial to know as much as possible about the properties of hydrogels in order to be able to use them in the most targeted way.

SYNTHESIS OF HYDROGELS

To characterize the hydrogels, the dimensionally stable PILs are being obtained by radical polymerization. An imidazolium-based ionic liquid bearing a vinyl group is polymerized with a crosslinker. Different crosslinkers, such as *N,N'*-Methylenebisacrylamide and Tri(ethylenglycol)divinylether, are used (Figure 1). There are several variations during synthesis, which have a decisive effect on the synthesis of the hydrogel, e.g. the content and type of crosslinker, water content and the ionic liquid monomer. At the same time, however, the properties of the hydrogel are of course also influenced by the variation. Another significant influence on the properties has the storage of the hydrogels, hence all experiments were performed with specimens, which were dried in a climatic chamber at a constant temperature of 25 °C and a relative humidity of 60% for different durations. All hydrogels were prepared in a specified size (d = 10 mm).

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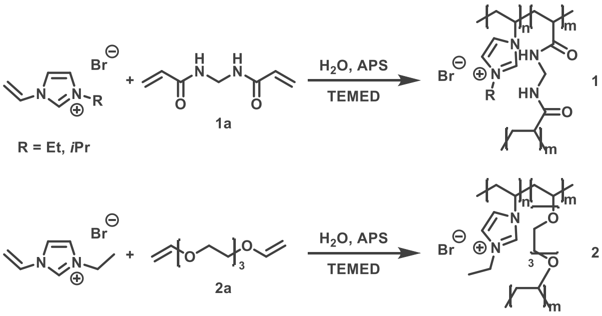

Figure 1: Radical polymerization of an imidazolium-based ionic liquid bearing a vinyl group, [VRIm][Br] – 1-Vinyl-3-alkylimidazolium bromide and cross-linker 1a *N,N'*-Methylenebisacrylamide (BisA); 2a Tri(ethylenglycol)divinylether (TEGDVE). APS – Ammonium peroxydisulfate, TEMED – *N,N,N',N'*-Tetramethylethane-1,2-diamine.

CHARACTERIZATION

Swelling Behavior

The swelling behavior of any polymer is significantly influenced by several factors such as the structure of the monomers used for hydrogel production, but also by the type and amount of crosslinker. Depending on the properties of the polymer network, the swelling behavior also changes with changes in external conditions, such as different solutions and solvents.

Table 1: Hydrogel - solvent combinations tested for swelling behavior at 23 °C.

Hydrogel \ Solvent	0.9% NaCl	0.1 M HCl	Ethanol	Acetone	Ethyl acetate
poly(VEImBr/BisA)	x	x			
poly(V*i*PrImBr/BisA)	x	x	x	x	x
poly(VEImBr/TEGDVE)	x				

Swelling measurements were performed in different solvents (Table 1) and analyzed gravimetrically. The drying conditions were 25 °C and 60% relative humidity (rh). The swelling ratio (SR) was determined as follows, as is common [Carvalho, 2013]:

$$SR = \frac{M_t - M_0}{M_0}. \tag{1}$$

In Figure 2, a solvent-dependent swelling and shrinking can be observed. In the aqueous solutions, the hydrogel swells significantly, with the greatest swelling observed in HCl. In the solvents ethanol, acetone and ethyl acetate the hydrogel shrinks, with swelling occurring in ethanol after 1440 min.

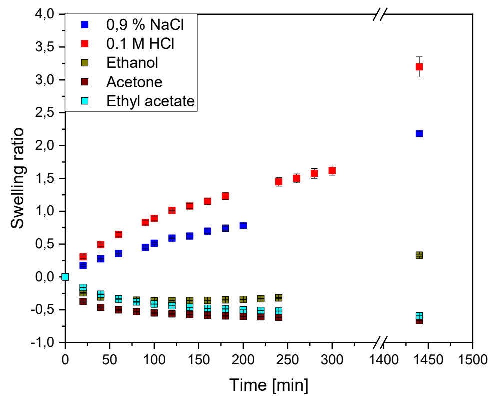

Figure 2: Swelling behavior of poly(V*i*PrImBr/BisA) hydrogels in different solvents at 23 °C.

That the swelling is not only dependent on the solvent, but also on the hydrogels respectively, IL monomers and crosslinkers used are shown in Figure 3. Here, a significantly higher swelling ratio can be observed with poly(VEImBr/TEGDVE). Poly(VEImBr/BisA) and poly(V*i*PrImBr/BisA) with the same crosslinker, show less difference in swelling behavior.

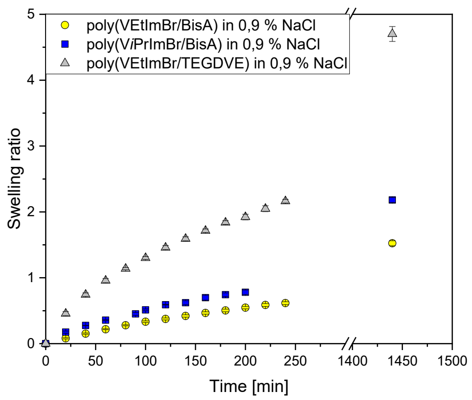

Figure 3: Swelling behavior of poly(VEImBr/TEGDVE), poly(VEImBr/BisA) and poly(V*i*PrImBr/BisA) in 0.9% NaCl solution at 23 °C.

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Mechanical Properties

Due to their high water content hydrogels possess generally a weak mechanical strength. However, the advantage of PILs-based hydrogels over e.g. alginate-based hydrogels is their significantly higher mechanical stability [Bandomir, 2014].

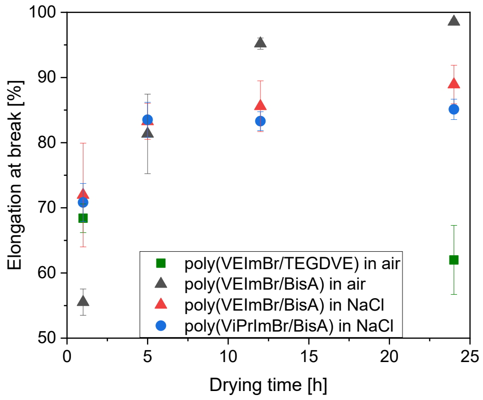

Figure 4: Elongation tests of poly(VEImBr/TEGDVE), poly(VEImBr/BisA) and poly(V*i*PrImBr/BisA) hydrogels with different degrees of drying at 25 °C and 60% rh partially in 0.9% NaCl solution with a loading speed of 0.1%/s.

The mechanical properties of poly(VEImBr/BisA), poly(V*i*PrImBr/BisA), poly(VEImBr/TEGDVE) were analyzed by means of elongation tests (Figure 4) and cyclic stress-strain relations (Figure 5). The influence of different drying times and also the influence of the surrounding medium (air or physiological saline solution) on mechanical behavior were investigated.

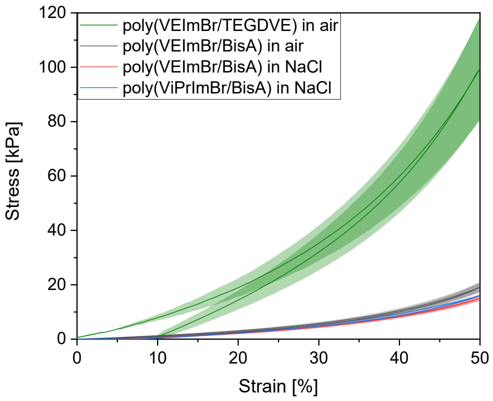

Figure 5: Cyclic stress-strain relation of poly(VEImBr/TEGDVE), poly(VEImBr/BisA) and poly(ViPrImBr/BisA) hydrogels with a drying time of 1 h at 25 °C and 60% rh partially in 0.9% NaCl solution with a loading speed of 0.1%/s.

The mechanical properties are affected by the IL monomer, composition, cross-linking density, degree of drying or swelling and drying method. Depending on the composition, they are compressible up to 98.5% without crack formation in the air and up to 88.9% in physiological saline solution. They show a reversible compression up to a strain increase of max. 8% for poly(VEImBr/TEGDVE) hydrogels. In comparison, the withstand stress differs significantly.

CONCLUSIONS

Stable PILs-based hydrogels were successfully synthesized by a radical polymerization. Two different ionic liquid monomers and two different crosslinkers were used. The swelling behavior and mechanical properties of the resulting hydrogels were analyzed. It was shown that the swelling behavior is solvent-dependent and depends on the composition of the hydrogel. The hydrogels exhibit high swelling behavior in aqueous media, while they shrink in organic media. The highest swelling ratio was observed in 0,1 M HCl. In a direct comparison in 0.9% NaCl solution of the different hydrogels, poly(VEImBr/TEGDVE) shows by far the greatest swelling ratio. The mechanical stability of the tested hydrogels has been extremely high, whereby the stability of the hydrogels increases with the drying time. The poly(VEImBr/BisA) hydrogel has shown a compression up to 98.5% without crack formation after 24 h drying time in the air and up to 88.9% in physiological saline solution and withstand a stress in the air up to 19.1 kPa. In comparison, poly(VEImBr/TEGDVE) hydrogels break slightly earlier, but withstand a much higher stress up to 99.6 kPa.

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NOMENCLATURE

APS Ammonium peroxydisulfate

Bis A *N,N'*-Methylenebisacrylamide

IL Ionic Liquid

M Mass [kg]

PILs Polymerized Ionic Liquids

rh relative humidity

SR Swelling Ratio

TEGDVE Tri(ethylenglycol)divinylether

TEMED *N,N,N',N'*-Tetramethylethane-1,2-diamine

VEImBr 1-Vinyl-3-ethylimidazolium bromide

V*i*PrImBr 1-Vinyl-3-*iso*propylimidazolium bromide

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